WE CLAIM:

1. A process for copper metallization comprising:

depositing a diffusion barrier comprising grain boundaries over a semiconductor substrate;

depositing a layer of a reactive metal over the diffusion barrier;

forming a different metal compound in the grain boundaries of the diffusion barrier; and

depositing a layer of copper over the diffusion barrier.

2. The process of Claim 1, wherein the diffusion barrier comprises a metal nitride.

3. The process of Claim 2, wherein the diffusion barrier comprises a metal nitride selected from the group consisting of titanium nitride, tungsten nitride and tantalum nitride.

4. The process of Claim 3, wherein the diffusion barrier comprises titanium nitride.

5. The process of Claim 2, wherein the reactive metal is selected from the group consisting of Al, Si, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mg, Y and La.

6. The process of Claim 5, wherein the reactive metal is Al.

7. The process of Claim 2, wherein the reactive metal is selected from the group consisting of metals of group IIIB of the periodic table, metals of group IVB of the periodic table, metals of group VB of the periodic table, and metals of Group VIB of the periodic table.

8. The process of Claim 2, additionally comprising incorporating nitrogen into the diffusion barrier prior to depositing the layer of reactive metal.

9. The process of Claim 2, additionally comprising incorporating oxygen into the diffusion barrier prior to depositing the layer of reactive metal.

10. The process of Claim 9, wherein incorporating oxygen into the diffusion barrier comprises annealing the substrate in the presence of oxygen.

11. The process of Claim 9, wherein incorporating oxygen into the diffusion barrier comprises treating the diffusion barrier with excited oxygen species.

12. The process of claim 2, further comprising depositing a second metal nitride layer between depositing the layer of reactive metal and depositing the layer of copper.

13. The process of Claim 9, wherein forming a different metal compound comprises forming metal oxide by annealing after deposition of the reactive metal layer.

14. The process of Claim 2, wherein forming a different metal compound comprises forming metal oxide by annealing in the presence of oxygen.

15. The process of Claim 14, wherein forming a different metal compound comprises forming metal oxide by annealing in the presence of oxygen after deposition of the second metal nitride layer and before depositing the copper layer.

16. The process of Claim 2, wherein the layer of reactive metal is deposited to a thickness of about 2 nm.

17. The process of Claim 2, wherein the metal nitride is deposited to a thickness of about 5 to 10 nm.

18. The process of Claim 2, wherein the metal nitride layer is deposited by atomic layer deposition (ALD).

19. The process of Claim 2, wherein the reactive metal layer is deposited by a process selected from the group consisting of chemical vapor deposition (CVD) and atomic layer deposition (ALD).

20. The process of Claim 2, wherein the reactive metal layer is deposited by plasma enhanced atomic layer deposition (PEALD).

21. A process for copper metallization comprising:

depositing a metal nitride layer on a semiconductor substrate;

depositing a layer of a reactive metal over the metal nitride layer, the reactive metal being different from metal in the metal nitride layer;

depositing a second metal nitride layer over the reactive metal layer; and

forming a metal compound in the grain boundaries of the metal nitride layers, the metal compound formed from the reactive metal.

22. The process of Claim 21, additionally comprising depositing a layer of copper directly over the second metal nitride layer.

23. The process of Claim 21, wherein the first metal nitride layer is titanium nitride.

24. The process of Claim 21, wherein the second metal nitride layer is titanium nitride.

25. The process of Claim 21, wherein the reactive metal layer is aluminum.

26. The process of Claim 21, wherein the reactive metal layer is silicon.

27. The process of Claim 21, wherein a layer of titanium is deposited over the reactive metal layer prior to depositing the second metal nitride layer.

28. The process of Claim 21, additionally comprising depositing a second metal layer over the reactive metal prior to depositing the second metal nitride layer.

29. A process of forming a barrier layer during semiconductor metallization comprising:

depositing a layer of titanium nitride in a damascene trench by atomic layer deposition (ALD);

depositing a layer of aluminum on the layer of titanium nitride; and

depositing a second layer of titanium nitride on the layer of aluminum.

30. The process of Claim 29, wherein the layer of aluminum is deposited by MOCVD.

31. The process of Claim 30, wherein the layer of aluminum is deposited from dimethylethylamine alane (DMEAA).

32. The process of Claim 29, wherein the layer of aluminum is deposited by plasma enhanced atomic layer deposition (PEALD).

33. The process of Claim 29, wherein the second layer of titanium nitride is deposited by atomic layer deposition (ALD).

34. The process of Claim 29, additionally comprising annealing in the presence of oxygen following deposition of the second layer of titanium nitride.

35. A diffusion barrier for a copper interconnect comprising a layer of metal nitride covered by a layer of reactive metal different from a metal in the metal nitride layer, wherein the grain boundaries of the metal nitride layer are stuffed with a metal compound of the reactive metal.

36. The diffusion barrier of Claim 35, wherein the metal nitride is selected from the group consisting of titanium nitride, tungsten nitride and tantalum nitride.

37. The diffusion barrier of Claim 36, wherein the metal nitride is titanium nitride.

38. The diffusion barrier of Claim 35, wherein the reactive metal is selected from the group consisting of Al, Si, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mg, Y and La.

39. The diffusion barrier of Claim 38, wherein the reactive metal is Al.

40. The diffusion barrier of Claim 38, wherein the reactive metal is Si.

41. The diffusion barrier of Claim 38, wherein the reactive metal is a lanthanide.

42. The diffusion barrier of Claim 35, wherein the reactive metal is selected from the group consisting of metals of group IIIB of the periodic table, metals of group IVB of the periodic table, metals of group VB of the periodic table and metals of group VIB of the periodic table.

43. The diffusion barrier of Claim 35, wherein the different metal compound is an oxide of the reactive metal.

44. The diffusion barrier of Claim 43, wherein the different metal is selected from the group consisting of aluminum oxide and silicon oxide.

45. The diffusion barrier of Claim 35, wherein the different metal compound is a nitride of the reactive metal.

46. The diffusion barrier of Claim 45, wherein the different metal is selected from the group consisting of aluminum nitride and silicon nitride.

47. The diffusion barrier of Claim 35, wherein the metal nitride layer is about 5 to 10 nm thick.

48. The diffusion barrier of Claim 35, wherein the reactive metal layer is about 2 nm thick.

49. The diffusion barrier of Claim 35, additionally comprising a second layer of metal nitride over the layer of reactive metal.

50. A diffusion barrier for a copper interconnect comprising:

a first layer of metal nitride;

a layer of reactive metal over the first layer of metal nitride; and

a second layer of metal nitride over the layer of reactive metal, wherein the grain boundaries of the first and second metal nitride layers are stuffed with a different metal compound.

51. The diffusion barrier of Claim 50, wherein the different metal compound is selected from the group consisting of an oxide of the reactive metal and a nitride of the reactive metal.

52. A diffusion barrier for a copper interconnect comprising a layer of titanium nitride covered by a layer of aluminum, wherein the grain boundaries of the titanium nitride layer are stuffed with aluminum oxide.

53. The diffusion barrier of Claim 52, wherein the layer of titanium nitride is deposited by atomic layer deposition (ALD).

54. The diffusion barrier of Claim 52, additionally comprising a second layer of titanium nitride between the aluminum layer and a copper filler.

55. A diffusion barrier for a copper interconnect comprising a layer of metal nitride covered by a layer of silicon, wherein the grain boundaries of the metal nitride layer are stuffed with silicon oxide.

56. The diffusion barrier of Claim 55, wherein the layer of metal nitride comprises titanium nitride.

57. The diffusion barrier of Claim 55, additionally comprising a second layer of metal nitride over the layer of silicon.

58. The diffusion barrier of Claim 57, wherein the second layer of metal nitride comprises titanium nitride.